Silicates

Oxygen and Silicon
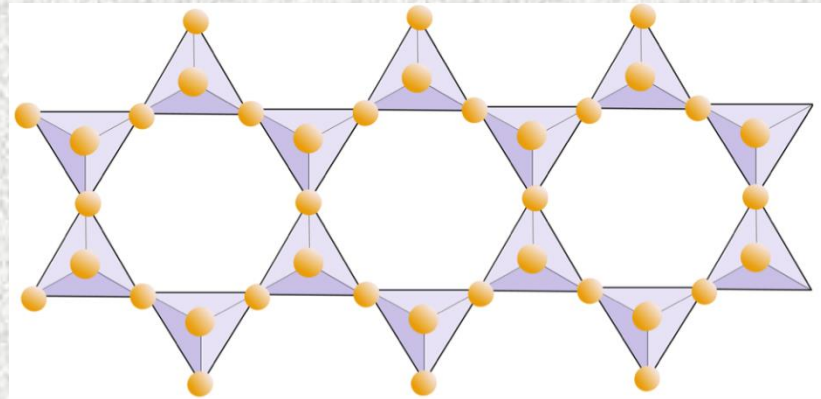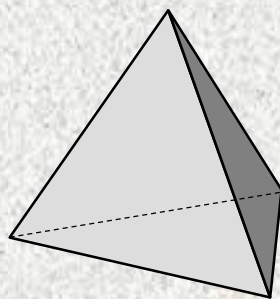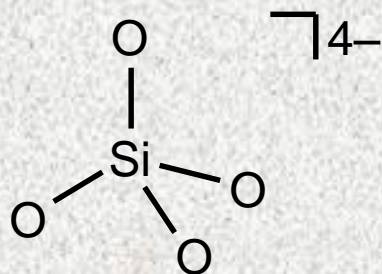
Oxygen and silicon – are the most abundant elements in the Earth's crust (49% and 26%, respectively).
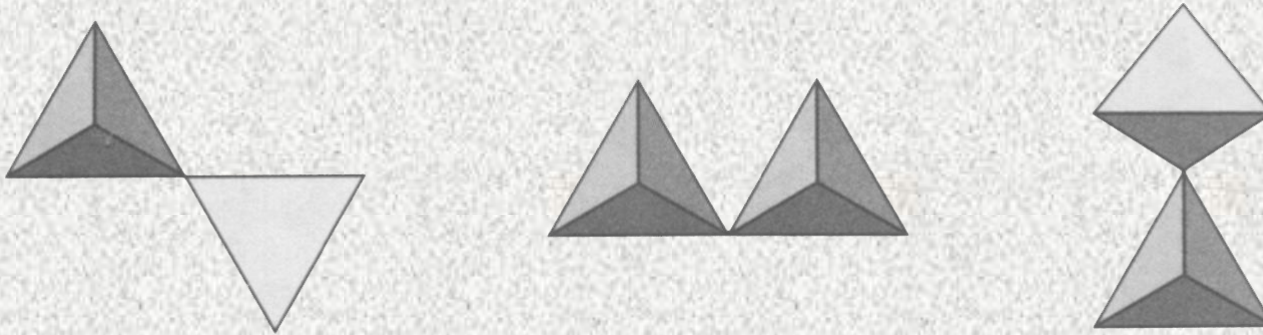
Oxides and silicates – are the most common minerals in Earth (silicates could be viewed as ternary oxides)

■ There are endless varieties of silicate structures, from monosilicates, to di-, tri-, oligo-, polysilicates with various dimensionalities and different structures.

■ Most silicates are amorphous and their detailed structures are unknown. There are some general structural features, however.
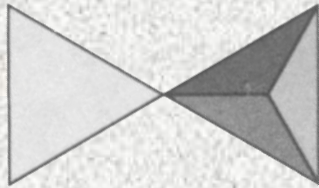
Monosilicate (SiO_4^{4-}) is the simplest silicate anion, having tetrahedral structure

Polysilicates

Silicate anions can be linked together through the corners (vertexes), but not edges or faces, due to strong Si^{4+}—Si^{4+} repulsion.
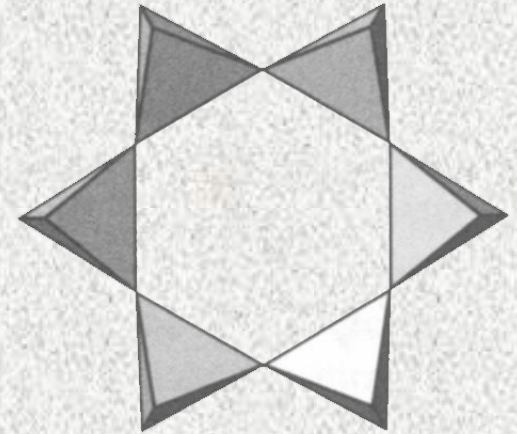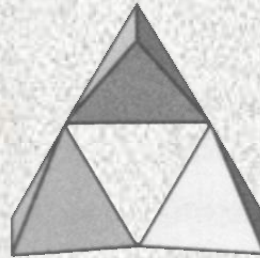

The connection between SiO_4^{2-} tetrahedra is quite flexible. Depending on the conformation of two tetrahedra in particular case, the angle Si—O—Si could vary from 180° to 102° (see picture).
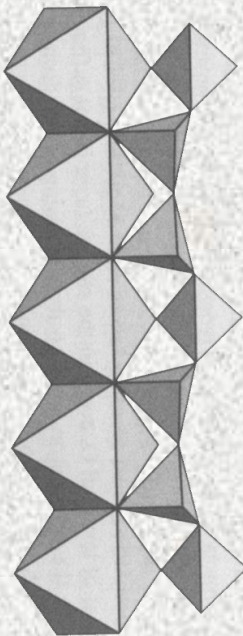
Structure of silicates in different dimensions

■ disilicate structure
in $Na_6Si_2O_7$.

■ cyclic tri- and hexa- silicate structures in benitoite $BaTiSi_3O_9$ and beryl $Be_3Al_2Si_6O_{18}$.

■ 1D chain of polysilicates (SiO_3^{2-}) in enstatite $MgSiO_3$ (left) and wollastonite $CaSiO_3$ (right). Note, that silicate chain geometry adopts to the size and geometry of the cationic chain.

■ 1D polysilicate ribbon $Si_4O_{11}^{6-}$ found in amphiboles.

Structure of silicates in different dimensions

■ some possible arrangements of tetrahedra in layered silicates.

In layered silicate structures the layers are not isolated but connected with each other through the O-vertices.

Structure of Mg(OH)$_2$ layer

Structure of Al(OH)$_3$ layer

Anionic silicate layer

The dot marks indicate the shared polyhedron vertices

Structure of layered silicates

Cation-poor silicate   Cation-rich silicate

The cationic layer could be connected with two silicate layer (cation-poor silicates) or one silicate layer (cation-rich silicates).
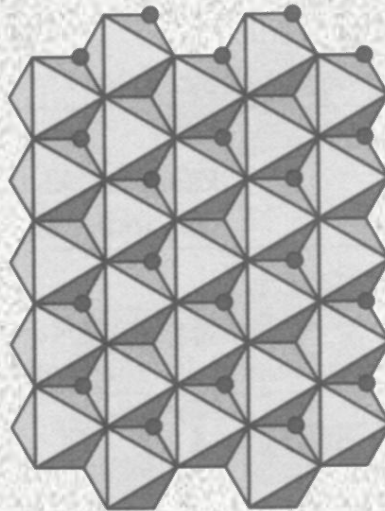
Depending on the metal type (Al or Mg), the number of silicate layers, the additional intercalated metal cations, protonation level, hydration level, etc, there are a lot of layered silicate structures (including micas, clays), most of which still are not well characterized structurally.

Some examples of layered silicates

cation layer	composition	examples
cation-rich silicates		
Al(OH)$_3$ type	M$_2$(OH)$_4${Si$_2$O$_5$}	kaolinite, Al$_2$(OH)$_4${Si$_2$O$_5$}
Mg(OH)$_2$ type	M$_3$(OH)$_4${Si$_2$O$_5$}	chrysolite, Mg$_3$(OH)$_4${Si$_2$O$_5$}
cation-poor silicates		
Al(OH)$_3$ type	M$_2$(OH)$_2${Si$_2$O$_5$}$_2$	pyrophyllite, Al$_2$(OH)$_2${Si$_2$O$_5$}$_2$
Mg(OH)$_2$ type	M$_3$(OH)$_2${Si$_2$O$_5$}$_2$	talc, Mg$_3$(OH)$_2${Si$_2$O$_5$}$_2$
cation-poor silicates with intercalations		
Al(OH)$_3$ type	A(M$_2$(OH)$_2${Si$_2$O$_5$}$_2$)	muscovite, K(Al$_2$(OH)$_2${AlSi$_3$O$_{10}$})
	A(M$_2$(OH)$_2${Si$_2$O$_5$}$_2$)·nH$_2$O	montmorillonite,
		Na$_x$(Mg$_x$Al$_{2-x}$(OH)$_2${Si$_2$O$_5$}$_2$)·nH$_2$O
Mg(OH)$_2$ type	A(M$_2$(OH)$_2${Si$_2$O$_5$}$_2$)·nH$_2$O	vermiculite, Mg$_3$(OH)$_2${Si$_2$O$_5$}$_2$·nH$_2$O

Crystalline three-dimensional SiO_2 structures

■ In 3D silica oxide the SiO_4 tetrahedra are connected through all four vertices, making the SiO_2 structure. Depending on the mutual orientation of the SiO_4 tetrahedra there are a number of known crystalline polymorphs (phases) of silica: *α*-quartz (rhombohedral) *β*-quartz (hexagonal), *α*-tridymite (orthorhombic), *β*-tridymite (hexagonal), *α*-cristobalite (tetragonal), *β*-cristobalite (cubic), moganite (monoclinic), coesite (monoclinic), stishovite (tetragonal), poststishovite (orthorhombic), and several else. These phases have different properties (melting point, hardness, density, refraction index, *etc*).

At normal conditions the stable phase for SiO_2 is *α*-quartz.

The structure of *α*-quartz

The *α*-quartz structure is chiral (therefore non-centrosymmetric) due to intrinsic helices. This explains certain quartz dielectric properties such as piezoelectricity.
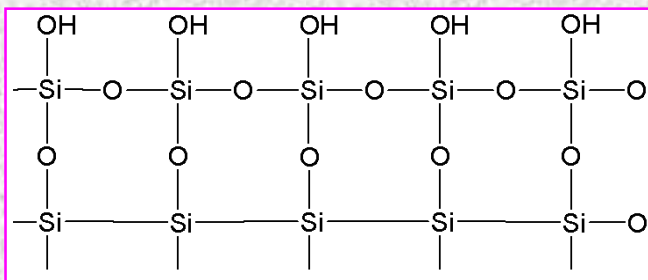
Amorphous three-dimensional SiO_2 structures

■ In the structure of amorphous glasses there is no long-range order in the packing of SiO_4 tetrahedra. There is, however, some short-range ordering, similar to known phases like *e.g.* quartz. Glasses are obtained when SiO_2 melt is solidified quickly.
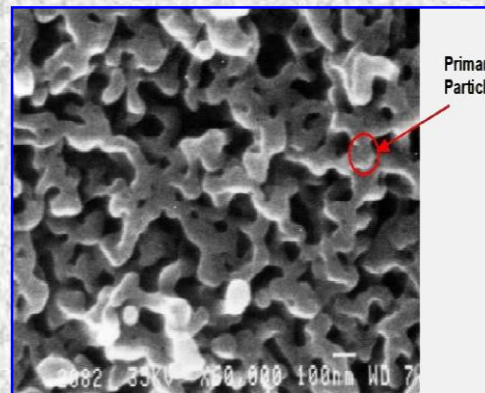
Other chemicals are used as additives to reduce the glass transition temperature of material (which is >1200 °C for pure SiO_2): Na_2CO_3, CaO, MgO, Al_2O_3, B_2O_3 (pyrex)

Some dopants alter glass properties: Pb^{2+} and Ba^{2+} increase refractive index and optical dispersion (lead glass); La^{3+} provides a high refractive index but low dispersion and used in optical lenses; Fe^{3+} glasses absorb IR light (used in heat absorbing filters)

■ Silica gel is another amorphous phase, obtained by acid hydrolysis of Na_2SiO_3 solution, followed by high temperature dehydration of gelatinous precipitate to make solid colorless gel. Silica gel has porous structure with submicron-size pores. It is commonly used as dehydration agents and porous sieves in chromatography.
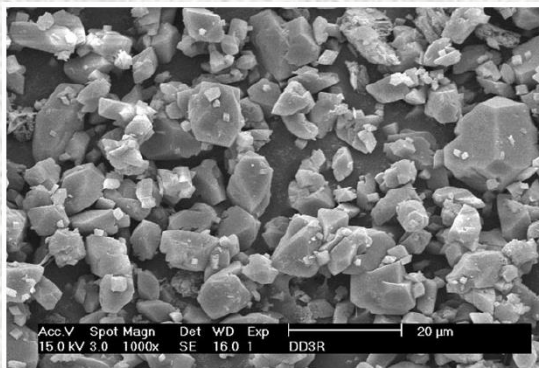
Schematic structure
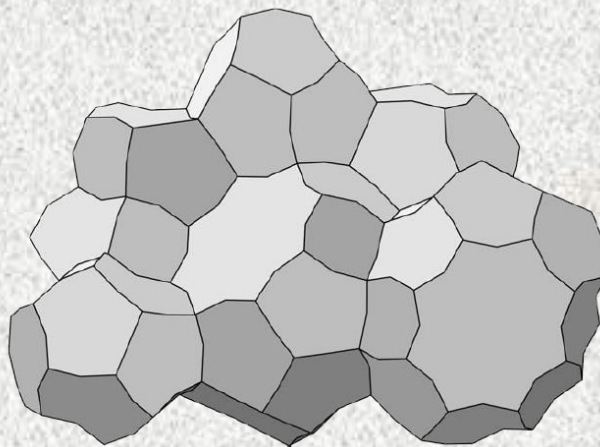of silica gel surface

Microstructure of silica-gel

Beads of silica gel

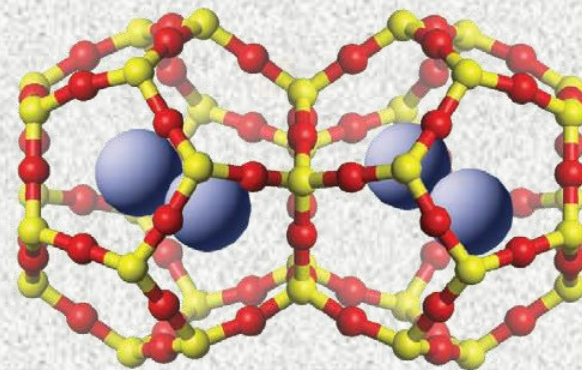# Porous three-dimensional SiO$_2$ crystalline structures

■ Hydrolysis of organisilicates (such as Si(OMe)$_4$) in a presence of some small organic templates or high pressure of some gases (N$_2$, CO$_2$, CH$_4$) leads to new 3D frameworks of SiO$_2$, where SiO$_4$ tetrahedra are linked together forming some cages around template molecules. These template molecules become permanently trapped inside the cages. Such templated porous silica structures are known as clathrasils. Structuraly they are very similar to clathrate hydrates.

SEM image of
clathrasil crystals

The packing of the clathrasil cages.
Si atoms are vertices, O atoms are
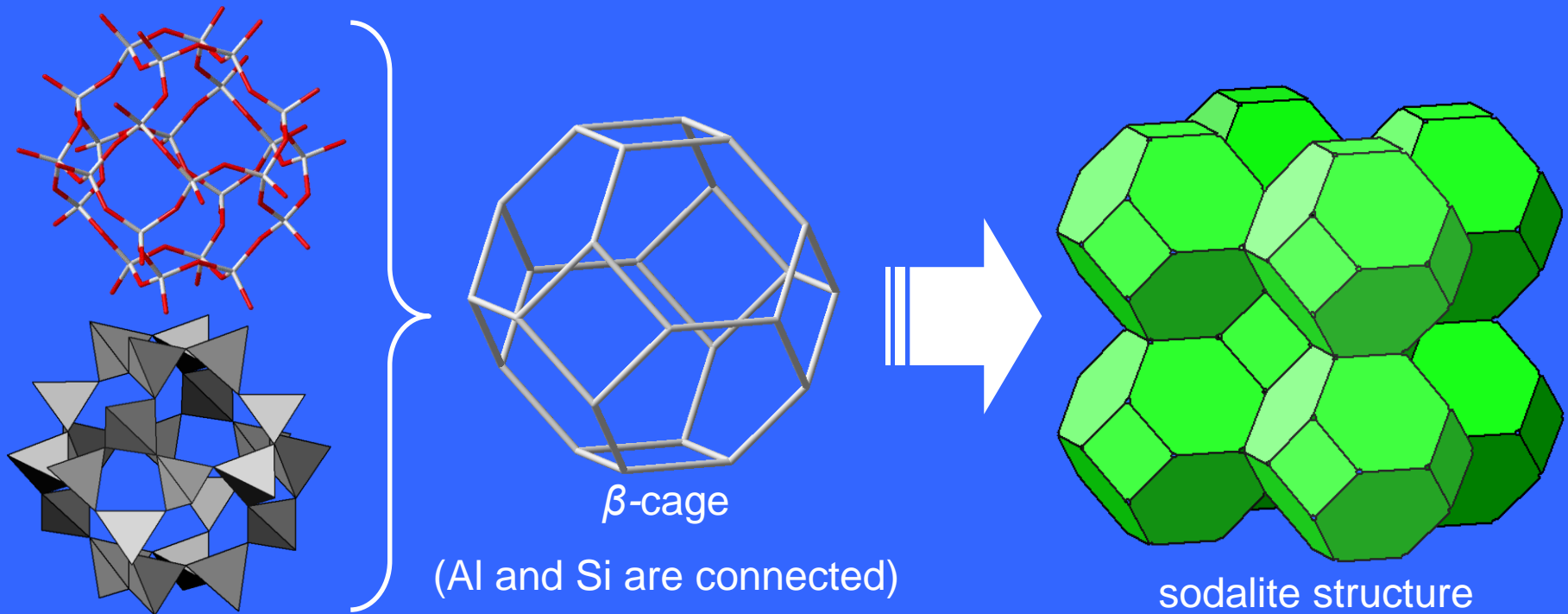edges of the polyhedral cages.

Structure of gas molecules
inside clathrasil cages.

Porous alumosilicates

Aluminum cation Al^{3+} is capable to form tetrahedral anions AlO_4^-, which could form solid solutions with silica tetrahedra SiO_4. The alumosilicates could be prepared by simultaneous precipitation of solid gel from solution of silicates and aluminates at decreased pH.

In such 3D structures each AlO_4 tetrahedron bears negative charge, therefore the general formula of alumosilicates is $M_x\{Al_xSi_yO_{2x+2y}\}$ (M = alkali metal or similar cation).

Example: $NaAlO_2 + Na_2SiO_3 + NaCl \longrightarrow Na_3\{Al_3Si_3O_{12}\}\cdot NaCl$ (sodalite)

β-cage

(Al and Si are connected)
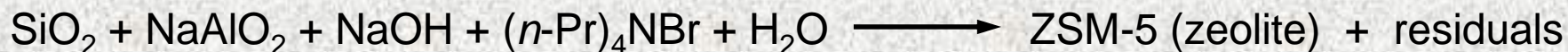
sodalite structure

Porous alumosilicates (zeolites)

In the synthesis of alumosilicates $M_x\{Al_xSi_yO_{2x+2y}\}$ various organic cations could also be used, instead of alkali metals as templates. These organic templates (structure-directing agents), direct the assembly of the Al/Si tetrahedra into a certain 3D topology. Alumosilicate frameworks are spacey enough to accommodate template and some solvent (water) molecules. Such porous alumosilicates are called zeolites. There are some zeolite minerals found in nature, however, synthetic zeolites have a much more important impact in materials chemistry and chemical industry.

Both Al and Si cations are randomly disordered in the alumosilicate structure. The alumosilicate framework is usually quite rigid and could maintain its porous structure after the removal of the organic template (organics is usually burned off at high temperatures in the presence of oxygen). The resulting porous zeolite has uniform narrow pores, which determine various properties and important applications of such materials.

Natural zeolite mineral

The zeolites are usually prepared in sol-gel synthesis at hydrothermal conditions:

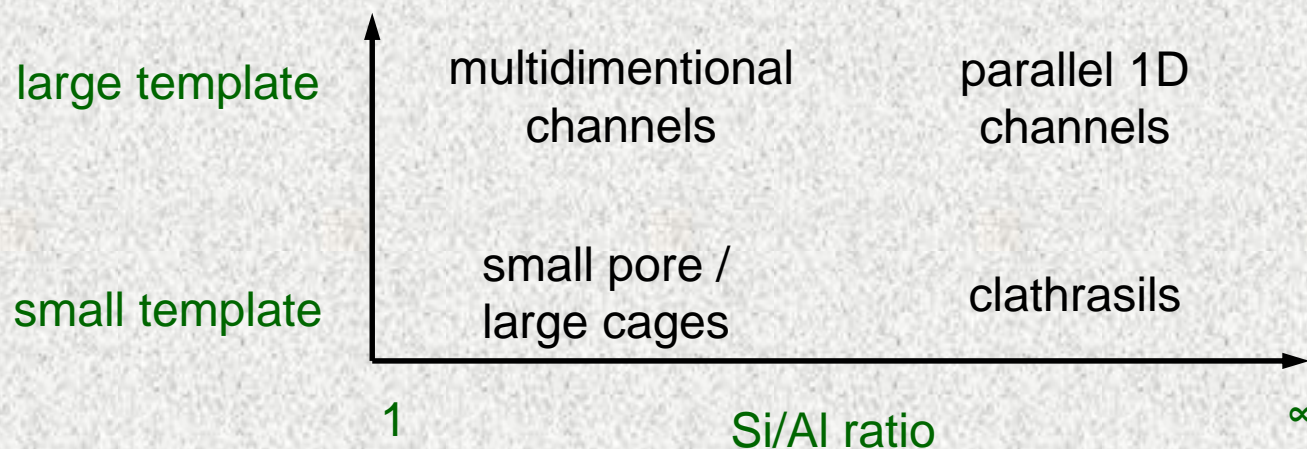SiO_2 + $NaAlO_2$ + $NaOH$ + (n-Pr)$_4$NBr + H_2O $\longrightarrow$ ZSM-5 (zeolite) + residuals
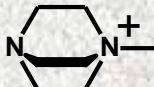
Zeolite Socony Mobil
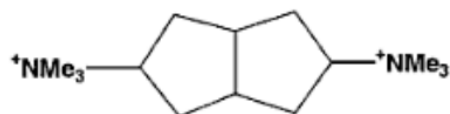
Control of the structures of zeolites

The porous structure of zeolites depends on the Si/Al ratio, template size, shape and charge, synthetic conditions (pH, temperature, concentrations). Also other tetrahedral anions and cations could be in the framework assembly: phosphates, gallates, *etc.*

large template — multidimentional channels — parallel 1D channels

small template — small pore / large cages — clathrasils

1 ← Si/Al ratio → ∞

Some frequently used organic templates: Me_4N^+; Et_4N^+; Pr_4N^+;

Example of the template effect on zeolite structure:

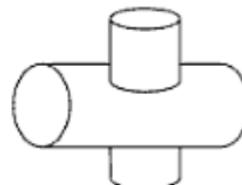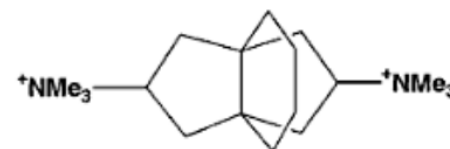linear template — $^+NMe_3$ ... $^+NMe_3$ **1** → 1D channel structure

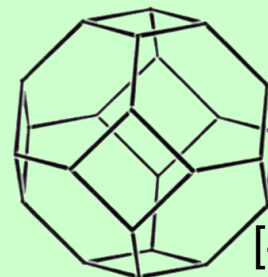bent template — $^+NMe_3$ ... $^+NMe_3$ → intersected channel structure

Some common building units of zeolites

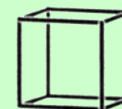Zeolite frameworks are composed of 4-connected, tetrahedral AlO_4/SiO_4 units (nodes).

Some common cage structures in zeolites:
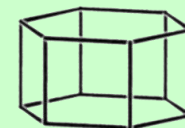*β*-cage (left), D4R (center), D6R(right).
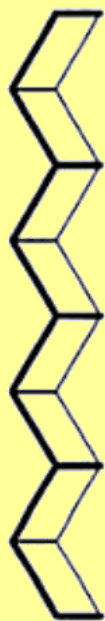
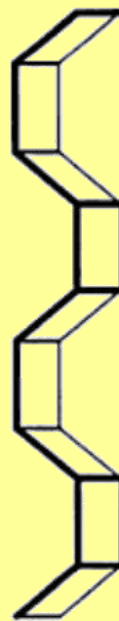Each corner represents Si/Al tetrahedron
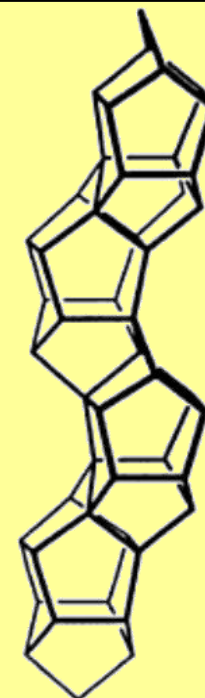
$[4^6.6^8]$ $[4^6]$ $[4^6.6^2]$

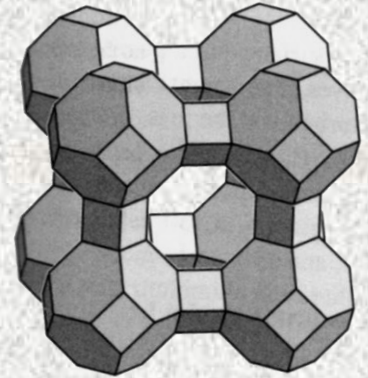| double zig-zag | double sawtooth | double crankshaft | Narsarsukite chain | pentasil chain |

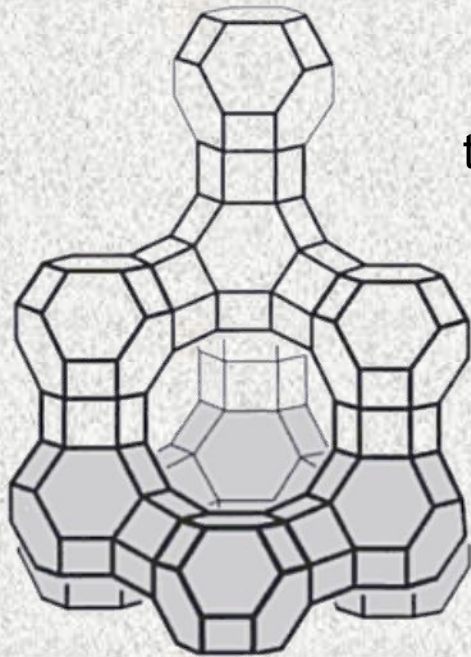Examples of 1D secondary building units in zeolites

Some common structural types of zeolites

■ In Zeolite A (**LTA** type) the β-cages are connected by D4R cages into cubic framework. The largest channel composed of 8 linking tetrahedra (8-member ring) and has the diameter 4.1 Å. The center of cubic porous structure constitutes α-cages [$4^{12}.6^8.8^6$].

Zeolite A

■ In Faujasite (**FAU**-type) the β-cages are connected by D6R cages into diamond-like (cubic) framework. The largest channel composed of 12 linking tetrahedra (12-member ring) and has the diameter 7.4 Å.

Zeolite X / Faujasite

■ In EMC-2 (**EMT**-type) the β-cages are connected by D6R cages into hexagonal lonsdalite framework. There are two different cages, connected by 12-member rings.
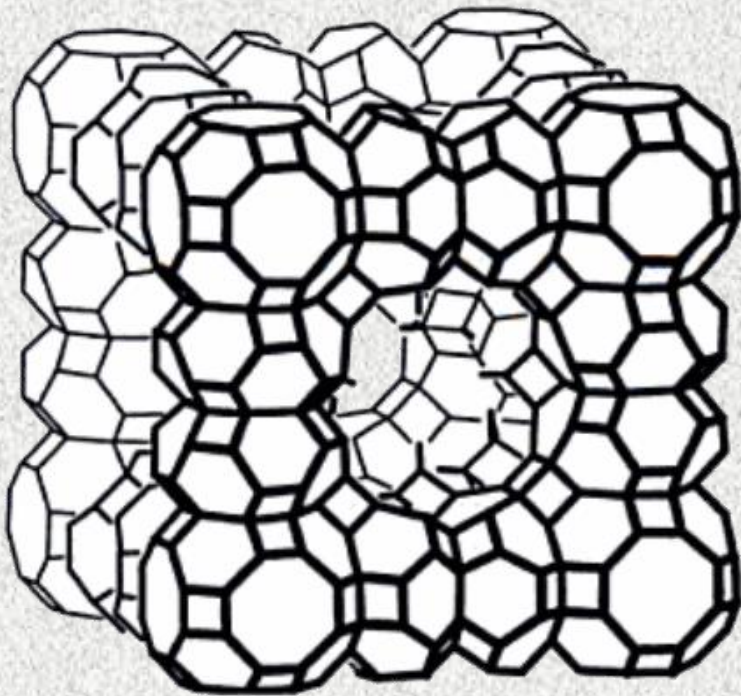
note: the polyhedra are actually empty!

EMC-2

Some common structural types of zeolites

■ **GIS**-type of zeolite framework. The framework is built from intersecting double crankshaft chains (shaded by gray), sharing one square face.

Example: Gismondine, $Ca_4(H_2O)_{16}[Al_{12}Si_{24}O_{72}]$

■ **CLO**-type of zeolite framework is represented by cloverite (gallium phosphate). The framework is built from α-cages connected by two smaller $[4^8.6^8.8^2]$ cages. The cavity inside the cubic unit cell is almost 3 nm (among the largest pore dimensions known in crystalline zeolytes). The channel cross-sections are 20-member rings (*ca*. 1.1 nm size).

Example: $(C_7H_{14}N)_{24}[Ga_{96}P_{96}O_{372}(OH)_{24}]F_{24}$

Some common structural types of zeolites

■ ■ **GME**-type and **CHA**-type of zeolite structures are built from D6R cages, connected by square rings. The difference is the packing of these cages: ABABAB for gmelinite and ABCABC for chabasite. The size of channels are comparable, however, the packing affects the channel shape.

Gmelinite, $Na_{12}[Al_{12}Si_{24}O_{72}] \cdot 33H_2O$

Chabasite, $Ca_6[Al_{12}Si_{24}O_{72}] \cdot 36H_2O$

Some common structural types of zeolites

■ ZSM-5 zeolite (**MFI**-type) is built from pentasil chains, which are connected *via* neighboring tetrahedra, forming straight channels across the pentasil chains. These straight channels intersect with another (zig-zag) channels. Both type of channels have 10-member rings.

Channels in ZSM-5 zeolite

Structure of ZSM-5 zeolite

Some common structural types of zeolites

Alumophosphate molecular sieves with structural types **AFI** (left) and **VFI** (right).

Examples of these framework types:

■ **AFI** = $AlPO_5$-5: $(C_{12}H_{28}N)_4(OH)(H_2O)_x[Al_{12}P_{12}O_{48}]$

■ **VFI** = VPI-5: $(H_2O)_{42}[Al_{18}P_{18}O_{72}]$

Synthesis of mesoporous molecular sieves

There are no large, water-soluble organic molecules, suitable for the templating of mesoporous (> 2 nm) zeolyte materials. The concept of the synthesis of mesoporous molecular sieves is based on a supramolecular templating.

hydrophobic tail, cationic head

array of rods

spherical micelle

micelle rod

SiO_2 precursor

silicate gel with porous structure

anionic gel between the cationic micelles

The structure of alumosilicate walls in mesoporous zeolites is believed to be amorphous.

Synthesis of mesoporous molecular sieves

Depending on the surfactant size and concentration, the channel diameter and shape could be controlled from 1.5 to *ca*. 10 nm, with hexagonal, cubic or lamellar arrangement of the channels.

Structural model of MCM-41

(hexagonal)

Structural model of MCM-48

(cubic)

Structural model of MCM-50

(lamellar)

"MCM" = Mobil Composition of Matter

Properties of porous zeolites

Due to the very uniform dimension and geometry of channels in porous zeolites, such structures demonstrate highly selective size- and shape-dependant sorption.

1 = N_2; 2 = *n*-heptane;
3 = propane; 4 = *i*-butane

Partial exchange of two Na^+ cations to one Ca^{2+} cation expands the effective diameter of channels in zeolite A ($Na_{12}[Al_{12}Si_{12}O_{48}]$) structure.

At the certain Ca^{2+} content pore size becomes large enough to allow the diffusion of small gases (N_2) or normal alkanes, but not branched alkanes (isobutane).
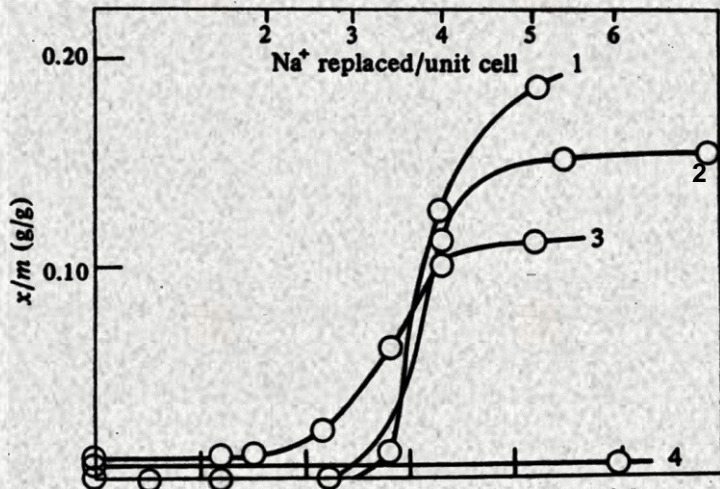
Temperature-dependant sorption of gases in NaA zeolite. At low temperature larger gases (N_2 and Ar) are not absorbed (very slow diffusion kinetic), while smaller O_2 is well absorbed. At intermediate temperatures the diffusion kinetics of N_2 and Ar becomes faster and hence some notable sorption is observed. At higher temperatures the sorption is always low due to thermodynamic effects as sorption is exothermic (actually more than a liquefaction).

Applications of porous zeolites. Ion exchange.

Alumosilicates are anionic frameworks, capable of exchange of cations.

$$Na_{12}[Al_{12}Si_{12}O_{48}] + 6Ca^{2+} \longrightarrow Ca_6[Al_{12}Si_{12}O_{48}] + 12Na^+$$

The reaction is used for softening the water.
Zeolites are usually added to detergents to
soften the water and maintain the ionic balance.

Water softening is the second major use for
zeolites (after petrochemical industry).

Zeolite A (NaA)

$Na_{12}[Al_{12}Si_{12}O_{48}]$

Zeolites could also be employed to remove radioactive long-live cationic isotopes
(^{137}Cs, ^{90}Sr) from water wastes, as well as ammonia cation form agricultural or
industrially polluted water.

Applications of porous zeolites. Acidic catalysis.

Many porous zeolites could be obtained as protonated structures (H^+ as a counter ion to anionic alumosilicate framework). Also, the metal countercations coul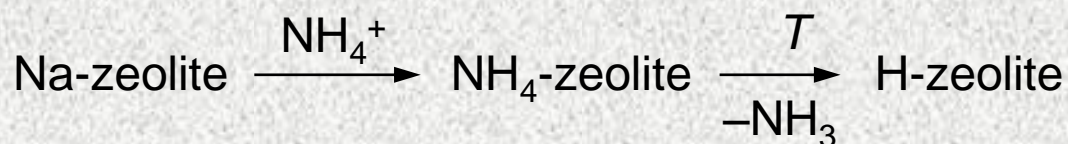d be substituted to H^+ (ammonium intermediates are used for those zeolites, which are unstable in acidic conditions):

$$\text{Na-zeolite} \xrightarrow{\ NH_4^+\ } \text{NH}_4\text{-zeolite} \xrightarrow[-NH_3]{\ T\ } \text{H-zeolite}$$
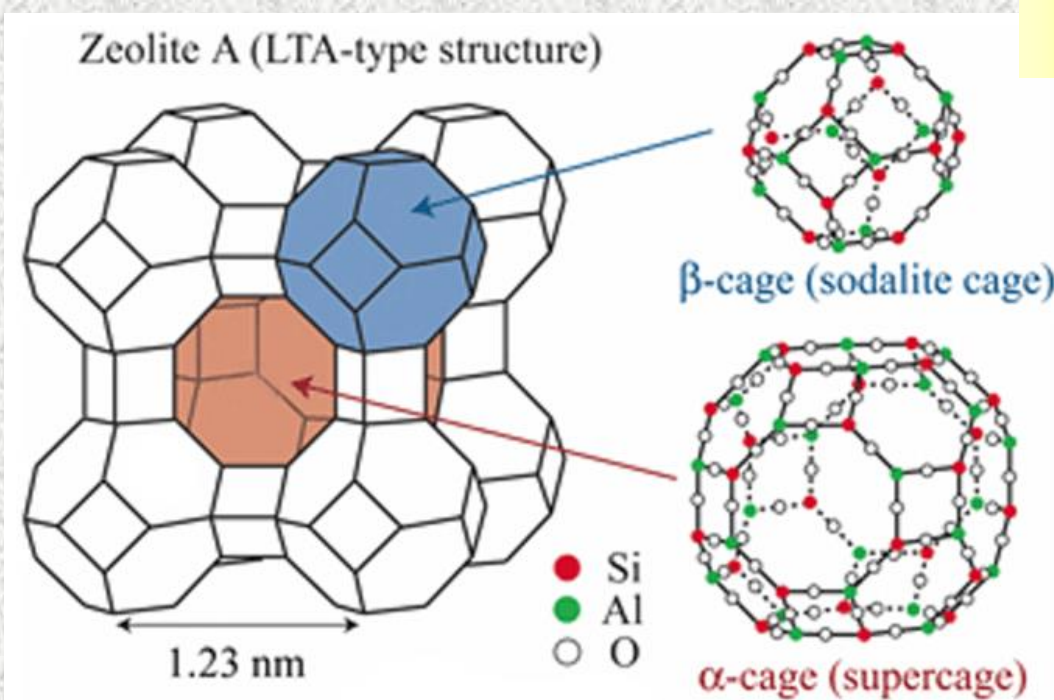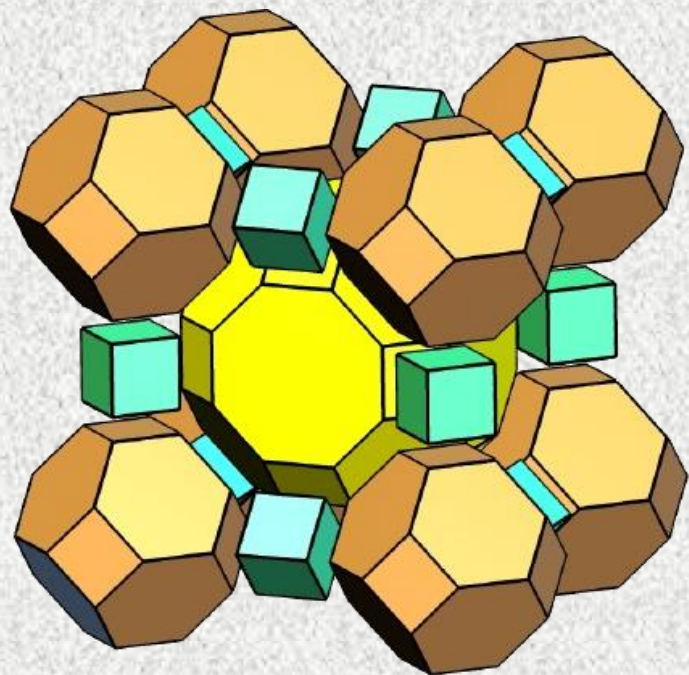
Acidic zeolites behaves as strong Brønsted acids (hydrated form) or Lewis acids (dehydrated form). Such acidic groups inside the porous structure acts as a very potent catalytic centers for acidic-promoted reactions. The catalytic use of zeolite materials is especially common and important for petrochemical industry (cracking, reforming, alkylation reactions, Friedel-Crafts reactions).

Almost all world's gasoline is prepared from refined oil using faujasite zeolite

The zeolite pores are uniform, therefore the catalytic activation is usually highly selective to reactant (only chemicals with particular size/shape could enter the zeolite pores and undergo the reaction, the others will remain unreacted) or product (only certain products could diffuse out of the channels and escape from the zeolite pores, while the others will continue to undergo the catalytic reactions).

Other catalytic applications of porous zeolites

■ Chabasite-type zeolites are used to activate the conversion of methanol to olefins, as well as aldol condensation of aldehydes.

■ The ZSM-5 zeolite is used to convert mixture of *o*-, *m*-, *p*- dimethylbenzenes to *p*-dimethylbenzene. The strongly acidic nature of ZSM-5 promote the catalytic isomerization of dimethylbenzenes, however, the pore structure of ZSM-5 allows only *p*-isomer (linear shape) to escape quickly from the zeolite structure. The non-linear *o*- and *m*-isomers are trapped inside and forced to undergo further protonation/izomerization, until the linear product is formed.

■ The mesoporous zeolites could be used as high-surface area support for some catalytically active complexes. The large nanoporous channels could also be modified by *e.g.* chiral complexes to promote stereoselectivity in sorption or catalytic properties.

■ The mild acidity of mesoporous H-MCM-41 combined with the large pores has been especially useful for carrying out reactions such as acetalyzations, Beckman rearrangements, glicosidation, and aldol condensation.

Zeolite A (LTA-type structure)

β-cage (sodalite cage)

α-cage (supercage)

1.23 nm

- Si
- Al
- O

Reticular Chemistry Structure Resource

http://rcsr.anu.edu.au